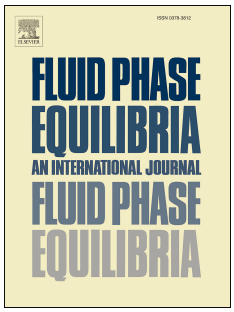


Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication

A. Marcilla, J.A. Reyes-Labarta, M.M. Olaya

PII: S0378-3812(16)30556-8

DOI: 10.1016/j.fluid.2016.11.009

Reference: FLUID 11319

To appear in: *Fluid Phase Equilibria*

Received Date: 21 June 2016

Revised Date: 3 November 2016

Accepted Date: 4 November 2016

Please cite this article as: A. Marcilla, J.A. Reyes-Labarta, M.M. Olaya, Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their assessment prior to publication, *Fluid Phase Equilibria* (2016), doi: 10.1016/j.fluid.2016.11.009.

Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication

A. Marcilla*, J.A. Reyes-Labarta and M.M. Olaya

Chemical Engineering Department, University of Alicante, Apdo. 99, 03080 Alicante, Spain.

*Corresponding author: Tel.: (34) 965 903789. E-mail: Antonio.Marcilla@ua.es.

Abstract

The review of a representative number of papers published in recent years that include the correlation of experimental liquid-liquid equilibrium (LLE) data has been carried out, after detecting serious inconsistencies in some of the parameters recently published. The result of this analysis shows that surprisingly many published parameters and calculated LLE data are inconsistent for different reasons, for instance: a) some parameters predict a type of system different from the experimental one, b) calculated tie-lines with the published parameters do not satisfy the Gibbs stability criteria, and c) in other cases do not even satisfy the isoactivity LLE condition. In most of these papers, the erroneous common final conclusion was a good agreement between the experimental and calculated tie-lines using these inconsistent parameters. Because these problems were not detected by the authors (when preparing the manuscript) nor by reviewers (during the review process), the necessity of a strategy for the validation of parameters (and compositions) calculated in LLE data fitting became evident. Such procedure should be applied to all LLE data correlation papers, prior to their publication in order to ascertain their consistency and quality. In this paper we suggest some possible tools that could be useful for this assessment.

Keywords: liquid-liquid equilibrium, LLE, correlation data, activity coefficient model, NRTL.

Introduction

Correlation data of multicomponent liquid-liquid equilibrium (LLE) is required in chemical engineering applications such as solvent extraction, and consequently it is a major issue in fluid phase equilibria calculations. Several authors, using different approaches, have dealt with this issue. In general, data correlation requires comparison between experimental and calculated equilibrium data. The accuracy of the results obtained in these correlations depends on many factors which are related to the quality of experimental data and how they are used, to the capability of the model selected, as well as to the robustness of the calculation algorithms to overcome the convergence problems related to them.

It is well known that the two more frequently used approaches for solving phase equilibria problems are the *K*-value method and the Gibbs energy minimization (GEM) method. The *K*-value method solves simultaneously a set of material balances and the isoactivity equilibrium condition for LLE given by

$$\text{O.F.(a)} = \sum_{j}^{nt}\sum_{i}^{nc}\left(a_{ij}^{I} - a_{ij}^{II}\right)^2 = 0 \qquad (1)$$

The calculated tie-lines are compared with the experimental ones by means of the concentration objective function:

$$\text{O.F.(x)} = \min \sum_{j}^{nt}\sum_{i}^{nc}\left[\left[(x_{ij}^{exp} - x_{ij}^{cal})^2\right]^{I} + \left[(x_{ij}^{exp} - x_{ij}^{cal})^2\right]^{II}\right] \qquad (2)$$

where i refers to each component, j to the tie-line, nt and nc to the total number of tie-lines and components, I and II to the two conjugated liquid phases in equilibrium and exp, cal to the experimental and calculated equilibrium data, respectively.

The Gibbs energy minimization method is frequently solved by means of the *Gibbs tangent plane test*, formulated theoretically by Gibbs more than 100 years ago. However, it was not until the contributions of Baker et al. [1] and Michelsen [2, 3] that the numerical implementation of the test was developed. A clear description of this subject can be found in the paper by Wasylkiewicz et al. [4]. Another example of implementation of this test in an algorithm for phase equilibrium calculations is the

computational tool developed by McDonald and Floudas [5]. According to the test, the necessary and sufficient condition for a phase with a given composition to be stable at fixed temperature and pressure, is that the Gibbs energy curve (surface or hyper-surface) of the mixture (G^M) is not intercepted by the tangent line (plane or hyper-plane) at the equilibrium points for a binary (ternary or multicomponent) system, respectively. In other words, for a ternary system this condition implies that the Gibbs tangent plane distance function, TPD(x), must be non-negative for any acceptable value of composition (x) and, consequently, when two or more phases coexist in equilibrium, one common tangent plane must exist in the equilibrium points that correspond with the minor value of the global Gibbs energy of mixing.

The *K*-value method is that most frequently used for LLE data correlation. For instance, this is the procedure used in Liquid-Liquid Equilibrium Data Collection DECHEMA Chemistry Data Series [6]. For binary systems, the *K*-value procedure provides acceptable results even with poor initial guesses, but for systems with a higher number of components, it can present some limitations widely discussed in literature [7]. As a consequence, the Gibbs energy minimization procedure could be preferable in these cases.

The most important limitations of the *K*-value method in its application to the correlation of LLE data are:

1. Isoactivity is a necessary but not sufficient condition for LLE.

The fulfillment of isoactivity does not guarantee the correct solution for the composition of the liquid phases in equilibrium because metastable solutions can exist that satisfying the isoactivity condition are not the stable solution for the system (minimum in the global Gibbs energy of mixing). The isoactivity condition is equivalent to the G^M common tangent line (plane or hyper-plane) for two, three or more components, respectively, but when more than one splitting is possible for a fixed initial global mixture, the unique stable solution is that corresponding with the minor global Gibbs energy (*Gibbs minor common tangent equilibrium criterion).*

2. Uncertainty in the isoactivity calculation

As shown in Figure 1(a) for a binary system, it would be desirable for the G^M function to give a proper definition of the two equilibrium points, which means that the

compositions with the lower common tangent line are precisely defined (x_1^I and x_1^{II} in this Figure). Nevertheless, the G^M function obtained in the LLE correlation, e.g. using the NRTL or UNIQUAC models, could be very linear between the two conjugated equilibrium points, depending on the values of the parameters of the model, as qualitatively shown in Figure 1(b) [8]. This poor definition of the LLE solution has dramatic consequences in the calculation of tie-lines, as we showed in paper [8], because extremely low values of the isoactivity criterion (as low as 10^{-12}) could not guarantee that the correct liquid compositions in equilibrium have been obtained. In other words, "false tie-lines" very far from the correct ones would appear to satisfy isoactivity equilibrium condition. Therefore, when the isoactivity criterion is used as the equilibrium condition, it is necessary to be very strict in the requirements for the activity equalities, specifically when we are dealing with very flat G^M functions.

3. Solutions are highly dependent on initial guesses.

The high non-linearity of the activity model equations as NRTL and UNIQUAC and the computational algorithm implemented for the optimization cause different parameter sets to be obtained as a result of a given correlation, all of them with similar values for the objective function represented in Eq. (2), in which experimental and calculated equilibrium data are compared. This problem is especially relevant in LLE due to the characteristics of this type of calculation where the activity of each component on both equilibrium liquid phases must be equated at equilibrium without knowing the experimental value for any of these activities. This fact makes the validation of the results difficult and limits the application of the parameters obtained by regression in predicting phase equilibria [9]. In this respect, we proposed a procedure [10] based on the second derivative of the G^M function to avoid many convergence problems, to decrease the possibility of multiple roots, and to minimize the dependence on the final results with the initial guesses. For particularly problematic cases with serious problems of convergence, we suggested the application of the vector method [8].

4. No guarantee of parameter consistency in all the composition space.

Parameters of the activity coefficient model are obtained by the correlation of experimental LLE data and as a consequence, there is no guarantee that these parameters respond to the behavior in the miscible regions of the system. For example,

in the Treybal classification [11] ternary LLE systems are grouped, according to the number of partially miscible binary subsystems (PMBS), into four types: type I (one PMBS), type II (two PMBS), type III (three PMBS) and type 0 or island (zero PMBS). When a set of experimental LLE ternary data is correlated with a model, it is not only very important to obtain a good agreement between experimental and calculated data, but also to guarantee that the parameters obtained are consistent with the type of system (type I, II, III or island for three components) being correlated. This means that the parameters must not only reproduce well the LLE splitting corresponding to the experimental tie-lines, but also the miscibility regions of the system including the miscible binary subsystems. There are two possibilities: a) to check the consistency after the correlation procedure is finished, or b) to introduce restrictions to the model parameter values into the optimization algorithm used for the correlation. This latter case presents a clear advantage that is the guarantee of consistency (in this regard) for the parameters obtained, avoiding trial and error procedures. In paper [12], we presented a polynomial relation between the NRTL binary parameters to ensure correct phase behavior among all the binary pairs involved in the ternary system during the correlation procedure. Obviously, an equivalent relation could be obtained for other activity coefficient models as UNIQUAC.

In recent years, addressing all these problematic aspects from different points of view, we have reviewed a substantial number of papers dealing with experimental LLE data correlation. Surprisingly, we found that a quite high percentage of these papers presented very relevant inconsistencies in their results. In the present paper, we are not concerned about the limitations of the activity coefficient models to describe the LLE data of many systems, which has been addressed extensively in many other papers, but in the discussion of frequent inconsistencies in the correlation results with the aim of encouraging authors, reviewers and editors to adopt some adequate procedure to avoid these kinds of problems. The analysis of the topology of the Gibbs energy of mixing function could have a relevant role in the solution to this problem.

Systems revised and inconsistencies detected

After we discovered some published papers where different type of inconsistencies appeared, a bibliographic search was carried out to determine the frequency of this inadequate procedure. We had no intention of finding all the papers with this kind of

problem neither make a statistical study but only to check the magnitude of the problem. With this aim in mind, we decided to review 25 papers randomly selected among those that had used NRTL to correlate experimental LLE data for ternary systems and included all the information required to perform this study. As sources of the data, we focused on some of the most relevant journals in this field: *Fluid Phase Equilibria*, *Chemical Engineering Data*, *Journal of Chemical Thermodynamics*, *Journal of Industrial and Engineering Chemistry*, and *DECHEMA Chemistry Data Series (vol. V).*

The 25 papers selected have been published in the last fifteen years, most of them in the last five years, and they included a total of 70 examples of LLE correlation because each paper includes several correlations for different ternary systems or for the same system at different temperatures. The activity coefficient model used in all these correlations was the NRTL equation, although we must point out that the model used has no relevance for the matter that is being discussed, and similar results could have been obtained using the UNIQUAC or any other model.

The results show that 13 of the 25 papers checked presented serious inconsistencies, which is 52 per cent. Since each paper sometimes includes the correlation of more than one system or the same system at different temperature conditions, the statistical taking into account the number of “examples” instead number of “papers” is also relevant. In this respect, 70 examples have been reviewed with a total of 42 presenting inconsistencies, which is 60 per cent. These results have been summarized in Table 1. Obviously any other sampling would provide other different figures, but what is relevant about these results is that real problems exist in this matter.

Although in some papers the inconsistencies are systematic, in other papers only a few tie-lines present some problem and the whole paper could still be considered valuable. We have decided to present a general statistical analysis to show the magnitude and characteristics of the problem, but without explicit mention of the references which contain this type of mistake. Obviously, this information has been provided to the editor and reviewers during the review process to give the required credibility to the present paper.

We have classified the inconsistencies in three types:

1. The model parameter values published do not correspond with the type of system being correlated, which means that they reproduce partial miscibility for binary subsystems that are totally miscible. For example, for type I ternary systems, the published parameters reproduce types II or III, and for type II systems parameters correspond with type III. In the present paper, this case is designed as *"binary subsystems (or type B) inconsistency"*.

2. In this group we consider *"tie-lines (or type T) inconsistency"*, in which the calculated LLE tie-lines obtained as regression result of the corresponding experimental ones are not consistent (do not satisfy the phase equilibrium criterion) with the model parameters published as a result of such regression. Within this group, we have also found two types of problems: a) the first one is due to metastable solutions, which means that the necessary but not sufficient isoactivity condition is satisfied by the calculated LLE tie-lines, but they do not correspond with the more stable situation for the system (the necessary and sufficient Gibbs minor common tangent test) (Type Ta in Table 1), and b) the second one are those examples that not even comply with the isoactivity condition (Type Tb in Table 1).

Within the type Ta inconsistences we have observed two different situations. The most frequent one is when the stable equilibrium solutions are LL tie-lines different from those published that are actually metastable solutions. However, another different and more complicated situation arises when type I or II systems are erroneously correlated with parameters leading to type III systems (type B inconsistency), thus producing at least one LLL tie-triangle in the ternary region that is more stable (less Gibbs energy of mixing) than the LL tie-lines published. This last situation occurs in examples 19 to 22, 41 and 57 (Table 1). In all these cases, the phase equilibrium diagram corresponding to the parameters obtained by the authors is more complex (i.e including several LL and LLL equilibrium regions) than the actual type I ternary system that it is being correlated (i.e including only a single LL equilibrium region).

To evaluate the type T inconsistencies, it would have been convenient if the papers included not only the values for the activity coefficient model parameters, but also the LLE compositions calculated by the authors themselves. Although papers including this information are scarce, this is not such an important limitation because when a good agreement between the experimental and model calculated compositions is found by the

authors, it is clear that both *exp* and *cal* LLE compositions must be quite close to each other. Consequently, an evident non-fulfilment of the equilibrium condition, as those that will be shown in the examples below, could not be justified by the difference between the experimental and calculated compositions.

3. A usually detected type of mistake consists of the use of mass fractions in the application of the original versions of the models, which actually require the use of molar fractions. Although this issue is often fixed during the review process, it can still be observed in the published articles. In Table 1 examples with this type of inconsistency have been labeled as *"mass"* (5 among 42 inconsistent examples).

Regarding the LLE correlation tools used by the authors of the reviewed papers, both commercial software and user programs including different algorithms and objectives functions have been used. For instance, in 12 of the examples checked, the authors have used Aspen Plus [13] for LLE data regression, presenting in 3 of them inconsistencies whose cause has not been identified. The validation of the correlation results obtained from commercial software seems to be convenient, as occurs when dealing with computer calculations in general.

The reasons for these errors could be in the algorithm itself, in the calculation procedure used by the author or simply a misprint in the results. We cannot know exactly the reason for the inconsistencies in all the examples analyzed, but we discuss as follows some ideas about this matter that could help to understand the problem. For instance, type B inconsistencies are quite frequent and occur because the real behavior of all the binary pairs is not imposed in the correlation algorithm nor validated after the correlation. In most cases, type T inconsistencies seem to be motivated by the incorrect application of the equilibrium conditions, e.g. metastable solutions and "relaxation" of the isoactivity condition are key factors that will be discussed below.

The utilization of inconsistent parameters could have severe consequences, e.g. when they are included in chemical process simulation software. Besides, any discussion on the capability of an activity coefficient model based on these inconsistent correlation results could be completely wrong, since the values of standard deviations or any other measurement of data fitting quality are completely unreliable, and this might erroneously influence the future work of research dealing with these topics. These aspects show the relevance of the issues discussed in the present paper.

We have selected some representative examples, among all those included in this study, to illustrate the previously discussed aspects.

Case 1

In a recent paper published in *J. Chem. Thermodynamics*, the authors presented the correlation of experimental LLE data for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) ternary system at T=298.15 K and atmospheric pressure (paper no. 1, example no. 1 in Table 1), using the NRTL model with the parameter values shown in Table 2a. The root-mean-square-deviation (RMSD) obtained was 0.006 and consequently, the authors concluded the good agreement of these results with the experimental data. These experimental compositions are represented in Figure 2 in a triangular plot, where it is shown that this is a Type I ternary system, based on the Treybal classification, where binary subsystems (1)-(2) and (1)-(3) are totally miscible (not LL splitting). However, the representation of the G^M/RT function obtained for each one of the three binary subsystems using the published parameters (Figure 3) shows that all of them are partially miscible. Specifically, the binary subsystem (1)-(2) that should be miscible shows two LL regions (two minor common tangents in Figure 3a), the binary subsystem (1)-(3) that should also be miscible shows one LL region (one minor common tangent in Figure 3b) and the binary subsystem (2)-(3), the only one with real partial miscibility, presents two LL regions instead of one (two minor common tangents in Figure 3c). Consequently, the paper analyzed in case 1 presents type B inconsistencies related with the lack of checking for the parameters obtained in the totally miscible binaries. Furthermore, what is more important, the isoactivity solution obtained by the authors is a metastable solution that does not satisfy the stability condition, this one leading to two LL tie-lines (common tangent lines in Figure 3c). The latter is a type T inconsistency in the binary (2)-(3), which propagates in the LL ternary region, as shown in Figure 4a where the calculated G^M/RT surface and the experimental LLE tie-lines have been represented versus the ternary composition for this same system. In this Figure, it is once again evident that experimental tie-lines are far from satisfying the LLE equilibrium conditions with the calculated parameters, for a similar reason to that discussed for the binary subsystem (2)-(3). Moreover, this idea is reinforced in Figure 4b, which presents the intersection to the ternary G^M/RT surface in the sectional plane defined by one of the experimental tie-lines, specifically that #9 (number increases with the molar fraction of (1)-component) is chosen only as an

example. It can be deduced from this Figure that the calculated tie-line which is being compared with the experimental one is a metastable solution that satisfies isoactivity but not the Gibbs stability condition for LLE. All the tie-lines presented in the paper show these type T inconsistencies among the experimental tie-lines and the parameters obtained due to metastable solutions. Consequently, the comments published in the paper on the good agreement between experimental and calculated tie-lines seem to be completely unfounded.

Case 2

In a paper published in *Fluid Phase Equilibria* in recent years, correlation results for LLE of the n-hexane (1) + benzene (2) + sulfolane (3) system at T=298.15K are reported (paper no. 19, example no. 58 in Table 1). The NRTL parameters published for this example are shown in Table 3a). The authors state literally that: "The parameters of the NRTL model have been successfully regressed from LLE data using the particle swarm optimization (PSO) method and smaller RMSDs (root-mean square deviations) were obtained compared with literature results". However, these model parameters provide all of the three binary subsystems partially miscible (type III ternary system) as shown in Figure 5a-c, whereas this system at the indicated conditions only has the (1)-(3) partially miscible binary pair (type I ternary system). From Figure 5b it seems that, without being aware of it, these authors could have obtained the metastable LL solution there indicated, which is close to the experimental solubility datum between the (1) and (3) components at the temperature of the system. However, the parameters given by them lead to other two stable LL regions for such a binary subsystem, which have been also drawn in the Figure. Moreover, Figure 6a shows the G^M/RT surface calculated by the NRTL model and in Figures 6b-d three sectional planes in the direction of three experimental tie-lines (#5, #7 and #9 increasing the molar fraction of benzene) have been represented. These Figures once again show the inconsistencies between the experimental tie-lines and the NRTL published parameters for this system. Therefore, both types B and Ta inconsistencies have been found for this case 2, the latter clearly due to metastable solutions of the isoactivity criteria.

Procedure suggested

The results and discussion presented in this paper seems to indicate the necessity of adopting an adequate strategy for validation of the parameters calculated in the LLE

data correlation prior to publication. So far, it appears that on many occasions reviewers are confident with the correct application of the procedures for LLE correlations by the authors and have no doubt about the consistency of the parameters reported (including possible errors as misprints, units,…) and consequently do not check such consistency and focus on other important aspects. However, the facts show that many papers report incorrect data and additional actions should be adopted to guarantee hereinafter the consistency of the published correlation results.

It would be advisable that the main journals in this field establish a commitment to perform this type of check. Previous examples of this type of action exist, as for instance the agreement signed in 2009 by five of these journals with the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST) [14] to the comparison with previous reported results. This agreement was the result of work begun in 2003. Chirico et al. published in 2013 a paper [15] to describe all the details, procedures and software tools, of this unique cooperation to improve the quality of published experimental data. Similarly, the improvement of the quality of the model parameters reported would require designing specific procedures, assessment tools and online support. In this sense, the journals and organizations as NIST will also play the main role.

In this paper, we propose some ideas that could be taken into account to implement such procedure. They are based on the topological information contained in the Gibbs energy of mixing function (G^M) to ensure the consistency of the calculated correlation parameters. The two types of checking, which have been previously discussed, should be carried out:

1. “Checking of binary subsystems (or type B) consistency”

The G^M curves for all the binary subsystems included in the system (e.g. three binary subsystems in ternary systems) must be inspected for consistency with the type of system. The type of system to be correlated with a model should be indicated by the authors of each paper (e.g. type I, II, III or island for ternary mixtures). For miscible binary subsystems no common tangent line to the G^M curve must exist, and for partially miscible ones one minor common tangent line must exist that corresponds with the calculated LLE tie-line, which could be close or far from the experimental one depending on the capacity of the G^E model to represent the system. This inspection

could be carried out by means of direct visualization or analytically obtaining the conditions for the model parameters values that reproduce totally miscible (L) or partially miscible (LL) behavior for binary systems, as proposed for the NRTL model in reference [12] where the mathematical function for this frontier was obtained. The type B inconsistencies are detected in a very simple way by the region in which the parameters are located. A similar study could be extended to other models as van Laar, Margules or UNIQUAC to obtain the corresponding mathematical functions for the parameter values frontier between LL and L regions. Another possible tool to check this kind of consistency related to the fulfillment of the type of system being correlated is the calculation of the solutions to the determinant of the Hessian matrix of the G^M function being equal to zero that gives the spinodal curve of the system [16]. This curve separates the intrinsically unstable and stable equilibrium regions showing all the LL regions reproduced by the parameters *in all the composition space* and not only close to the experimental tie-lines correlated, as is common practice. This procedure would clearly indicate the type of system that is generated by the parameters, allowing the detection of possible inconsistencies. It is obvious that this practice is more time consuming than only checking the binary subsystems, but it goes further allowing the detection of non-existing ternary LL regions such as type island ones, which would not be detected if only the binary subsystems were checked.

2. “Checking of tie-lines (or type T) consistency”

The consistency between the calculated tie-lines and the G^M surface obtained with the parameters should be analyzed in the complete heterogeneous region in accordance with the Gibbs minor common tangent equilibrium criteria. Taking into account that this criteria for ternary systems involves checking the position of common tangent planes to the G^M surface in the two conjugated liquid phases and the difficulties for the analysis of three-dimensional figures, we recommend the joint use of sectional planes to the G^M surface in the direction of the tie-lines (to check the fulfillment of the Gibbs criteria in two dimensions), and the visualization of the ternary G^M surface as an additional guarantee of its proper topology. Tie-lines used in this check would be the ones calculated by the authors themselves when they are available. Otherwise, the experimental ones could be used only if a good agreement between both sets of data is confirmed by the authors, and obviously a small margin for the Gibbs stability criteria

fulfillment should be assumed in this case by the small difference between experimental and calculated compositions.

Based on these ideas we have developed a simple but very useful tool, using a Graphical User Interface [17] written in MatLab® software code, to systematically check all the examples in the present study, which has allowed very easy detection of the inconsistencies discussed. Because this, or other similar, procedure to check the correlation results seems to be necessary, it could be mandatory for the authors themselves to apply such procedure to their results and submit the report obtained along with the manuscript. Other possibility would be that the journal itself (or the reviewers) were responsible for performing this check, for example after peer review but before acceptance for publication, as in the agreement previously cited [14, 15] to improve the quality of experimental data.

To complete this study, for cases 1 and 2, we have performed the LLE regression in order to obtain consistent sets of NRTL parameters as alternatives to the ones published. In Tables 2b and 3b these new sets of parameters are presented along with those previously published. We have checked the consistency of these three sets of parameters. For example, in Figures 7 and 8 we show the consistency of the parameters obtained for case 1 by means of the representations proposed in this section. In Figure 7, it is observed that only the 2-3 pair splits into two liquid phases as expected. Figure 8 shows the consistency between the calculated tie-lines and the G^M/RT surface obtained by the calculated parameters (Figure 8a) and for example, the projection on the sectional plane in the direction of one specific tie-line (#9) (Figure 8b). At this point, it is interesting to observe the comparison between Figure 4b (metastable solution) and Figure 8b (stable solution presented in this paper) for the same tie-line (#9). All the ternary tie-lines calculated as a result of the correlations for cases 1 and 2 have been checked, obtaining consistent common tangent lines among the conjugated liquid phases for all of them.

Conclusions

This study reveals the necessity of designing a strategy for the validation of the parameters and compositions calculated, specifically in LLE data fitting, which should

be applied prior to publication, for instance during the reviewing process by the journal or otherwise demonstrated by the authors themselves in the required way.

Every researcher working in this and any experimental area is not completely safe from possible mistakes, misprints, errors and so on, but it is clear that all of us would prefer being free of them. Besides, not all of the researchers working in the experimental field are similarly familiar with the correlation procedures, the stability conditions as well as other aspects affecting the quality of the calculated data because some of them present the correlation results as a complement of their experimental work. For all these reasons, it would be convenient if the different journals publishing this type of research could guarantee the top quality of the correlations and corresponding parameters, ascertaining the consistency with the behavior of the system, in the same way that they strive to ensure the top quality of the experimental data published.

We suggest some possible tools that could be useful for this assessment but it would be advisable that the main journals in this field establish a commitment to assure that this type of check is performed. Previous examples of this type of agreement exist, as that signed in 2009 by five of these journals with the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST) [14, 15], to the comparison with previous reported results. In paper [15] it is concluded that approximately one-third of articles reporting experimental data in this field contained mistakes before the agreement. The magnitude of the problem related to inconsistencies of the published model parameters could be of the same order of magnitude.

The topological information contained in the Gibbs energy of mixing (G^M/RT) function has demonstrated to be a very useful tool to ensure the consistency of the correlation parameters obtained. For ternary systems, the analysis of the calculated G^M/RT surface and G^M/RT curves in planes containing all the tie-lines could be a useful tool to validate the model parameters obtained, in agreement with the Gibbs stability equilibrium condition (minor common tangent plane test for ternary systems).

In addition, the restriction on the model parameter values during the correlation procedure (for ternary or higher systems) is convenient to guarantee the adequate prediction of the totally miscible binary subsystems, avoiding other tedious trial and error alternatives to ensure such consistency, which is in fact obviated in most of the cases. In the present paper, the mathematical function that limits the NRTL parameter

values corresponding with the LL and L regions has been applied for that purpose and similar functions could be deduced for other activity coefficient models.

An additional check could be the calculation of the spinodal curves of the system using the Hessian matrix. This is a more laborious but more complete procedure of checking that could reveal some not as frequent but possible inconsistencies, such as the detection of non-existing ternary LL regions (island type). This problem would not be detected if only the binary subsystems, and the calculated tie-lines obtained using the parameters close to the experimental ones, were revised.

References

[1] L.E. Baker, A.C. Pierce, K.D. Luks, SPE Journal, 22 (1982) 731-742.

[2] M.L. Michelsen, Fluid Phase Equilib., 9 (1982) 1-20.

[3] M.L. Michelsen, Fluid Phase Equilib., 9 (1982) 21-35.

[4] S.K. Wasylkiewicz, L.N. Sridhar, M.F. Doherty, M.F. Malone, Ind. Eng. Chem. Res. 35 (1996) 1395-1408.

[5] C.M. McDonald, C.A. Floudas, Computers chem. Engng. 21 (1) (1997) 1-23.

[6] W. Arlt, M.E.A. Macedo, P. Rasmussen, J.M. Sorensen, Liquid-Liquid Equilibrium Data Collection. Chemistry Data Series; Vol. V, DECHEMA: Frankfurt.

[7] G. Iglesias-Silva, A. Bonilla-Petriciolet, P. T. Eubank, J.C. Holste, K.R. Hall, Fluid Phase Equilib. 210 (2003) 229-245.

[8] M. M. Olaya, I. Ibarra, J. A. Reyes-Labarta, M. D. Serrano, A. Marcilla, Chem. Eng. Edu., 41 (3) (2007) 218-224.

[9] J.M. Prausnitz, R.N. Lichtentaler, E. Gomes De Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 3^{d} Edition, Pentice-Hall, 1999.

[10] J.A. Reyes-Labarta, M.M. Olaya, R. Velasco, M.D. Serrano, A. Marcilla, Fluid Phase Equilib., 281 (2009) 9-14.

[11] Treybal, R. E, Liquid Extraction, 2nd Ed. McGraw-Hill (1963).

[12] A. Marcilla, M. M. Olaya, M. D. Serrano, J. A. Reyes-Labarta, Ind. Eng. Chem. Res, 49 (20) (2010) 10100–10110.

[13] ASPEN-PLUS Chemical Process Optimization Software, Aspen Technology Inc.: Cambridge, MA.

[14] P.T. Cummings, Th.W. de Loos, J.P. O'Connell, Fluid Phase Equilib. 276 (2009) 165-166.

[15] R.D. Chirico, M. Frenkel, J.W. Magee, V. Diky, C.D. Muzny, A.F. Kazakov, K. Kroenlein, I. Abdulagatov, G.R. Hardin, W.E. Acree Jr., J.F. Brenneke, P.L. Brown, P.T. Cummings, T.W. de Loos, D.G. Friend, A.R.H. Goodwin, L.D. Hansen, W.M. Haynes, N. Koga,j A. Mandelis, K.N. Marsh, P.M. Mathias, C. McCabe, J.P. O'Connell, A. Pádua, V. Rives, C. Schick, J.P. Martin Trusler, S. Vyazovkin, R.D. Weir, J. Wu, J. Chem. Eng. Data, 58 (2013) 2699-2716.

[16] A. Marcilla, J.A. Reyes-Labarta, M.D. Serrano, M.M. Olaya, Ind. Eng. Chem. Res, 51 (2012) 5098−5102.

[17] J.A. Reyes-Labarta, Graphical User Interface (GUI) for the representation of G^M surfaces (using the NRTL model) and curves, including tie-lines and Hessian matrix, Institutional Repository of the University of Alicante (RUA) http://hdl.handle.net/10045/51725

Table 1. Ternary systems checked for consistency of the NRTL parameters published as result of the LLE data correlation.

No. paper	System	T (K)	No. example	Checking Result	Type of Inconsistency(*)
1	Benzene + cyclohexane + dimethyl sulfoxide	298	1	Not OK	B, Ta
		303	2	Not OK	B, Ta
2	Water + tetrahydrofuran + methylcyclohexane	278	3	OK	---
		288	4	OK	---
		298	5	OK	---
		323	6	OK	---
3	Dichloromethane +water +N,N Dimethylacetamide	298	7	Not OK	B, Tb
		308	8	Not OK	B, Tb
4	1-pentanol + 2-methyl-1-propanol + water	298	9	Not OK	Tb
		323	10	Not OK	Tb
		348	11	Not OK	Tb
5	1-butanol + 3-methyl-1-butanol + water	298	12	Not OK	B, Tb
		333	13	Not OK	B, Tb
		368	14	Not OK	B, Tb
6	2-methyl-1-propanol + 2-propanol + water	298	15	OK	---
		323	16	OK	---
		348	17	OK	---
7	Water + 1-butanol + p-xylene	313	18	OK	---
8	Water + acetic acid + cyclohexanone	293	19	Not OK	B, Ta
		303	20	Not OK	B, Ta
		313	21	Not OK	B, Ta

		323	22	Not OK	B, Ta
9	Water + toluene + benzaldehyde	303	23	Not OK	B, Tb
		313	24	Not OK	B, Tb
		323	25	Not OK	B, Tb
		333	26	Not OK	B, Tb
		34	27	Not OK	B, Tb
10	Isooctane + o-xylene + methanol	283	28	Not OK	B
		298	29	Not OK	B
		308	30	OK	---
	Isooctane + m-xylene + methanol	298	31	OK	---
	Isooctane +ethylbenzene + methanol	298	32	OK	---
11	Water + methanol + methyl acetate	283	33	OK	---
		303	34	OK	---
12	Water + lactic acid + 1-butanol	298	35	Not OK	Mass
	Water + lactic acid + 2-butanol	298	36	Not OK	Mass, B, Tb
	Water + lactic acid + 1-pentanol	298	37	Not OK	Mass
	Water + lactic acid + 1-hexanol	298	38	Not OK	Mass
	Water + lactic acid + 1-heptanol	298	39	Not OK	Mass
13	Water + 1-butanol + toluene	313	40	OK	---
14	Formic acid + water + 1-butanol	298	41	Not OK	B, Ta
	Formic acid + water + 1-pentanol	298	42	OK	---
	Formic acid + water + 1-hexanol	298	43	Not OK	B, Tb
	Formic acid + water + 1-heptanol	298	44	OK	---
15	Methanol + isooctane + cyclohexane	303	45	OK	---
16	Isooctane + benzene + methanol	298	46	OK	---

17	Heptane + benzene + methanol	293	47	OK	---
	Heptane +ethylbenzene + methanol	293	48	OK	---
	Heptane + m-xylene + methanol	293	49	OK	---
18	Water + octane + 2-butyloxy-ethanol	283	50	OK	---
		293	51	Not OK	Tb
		303	52	Not OK	Tb
		298	53	Not OK	Tb
		291	54	Not OK	Tb
19	Ethene tetrachloro + 2-propanol + water	303	55	Not OK	B
	Heptane + ethylbenzene + methanol	293	56	OK	---
	Cyclohexane + enthylbenzene + sulfolane	303	57	Not OK	B, Ta
	n-Hexane + benzene + sulfolane	298	58	Not OK	B, Ta
	Benzene isopropyl + 2-propanone + formic acid amide	298	59	Not OK	Ta
	Ethene tetrachloro + 2-propanone + water	303	60	Not OK	B, Ta
	Ethene trichloro + hexanoic acid 6-amino lactam + water	313	61	Not OK	B, Ta
20	Cyclohexane + ethylbenzene + sulfolane	303	62	OK	---
21	n-Hexane + benzene + sulfolane	298	63	OK	---
22	Propylbenzene + hexadecane + [mebupy][BF4]	313	64	OK	---
	Benzene + hexane + [3-mebupy][DCA]	303	65	OK	---
23	Hexadecane + propylbenzene + (mebupy)(BF4)	313	66	OK	---
24	Benzene + hexane + [3-mebupy][DCA]	303	67	Not OK	B, Ta
		328	68	Not OK	B, Ta
25	Dichloromethane +water +N,N Dimethylacetamide	298	69	Not OK	B, Tb
		308	70	Not OK	B, Tb

(*) Nomenclature for the type of inconsistency in “Systems revised and inconsistencies detected” section

Table 2. NRTL binary parameters (J/mol) obtained in the correlation of LLE data for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (3) ternary system at T=298.15 K (case 1).

a) Published (inconsistent)				
i	j	A_{ij}	A_{ji}	α_{ij}
1	2	12763.4	24786.4	0.4248
1	3	9587.29	-1688.07	0.3458
2	3	24220.8	11347.3	0.3750
b) Obtained in the present paper				
i	j	A_{ij}	A_{ji}	α_{ij}
1	2	-6741.27	7275.32	0.2
1	3	1050.97	6970.21	0.2
2	3	13545.2	4016.58	0.2

Table 3. NRTL binary parameters (J/mol) obtained in the correlation of LLE data for the n-hexane (1) + benzene (2) + sulfolane (3) ternary system at T=298.15K (case 2).

a) Published (inconsistent)				
i	j	A_{ij}	A_{ji}	α_{ij}
1	2	22761.7	8478.03	0.44505
1	3	19822.8	13937.4	0.42441
2	3	8194.48	1774.24	0.49549
b) Obtained in the present paper				
i	j	A_{ij}	A_{ji}	α_{ij}
1	2	-1668.78	5315.17	0.73115
1	3	6495.50	7615.40	0.10680
2	3	860.391	4924.17	0.99993

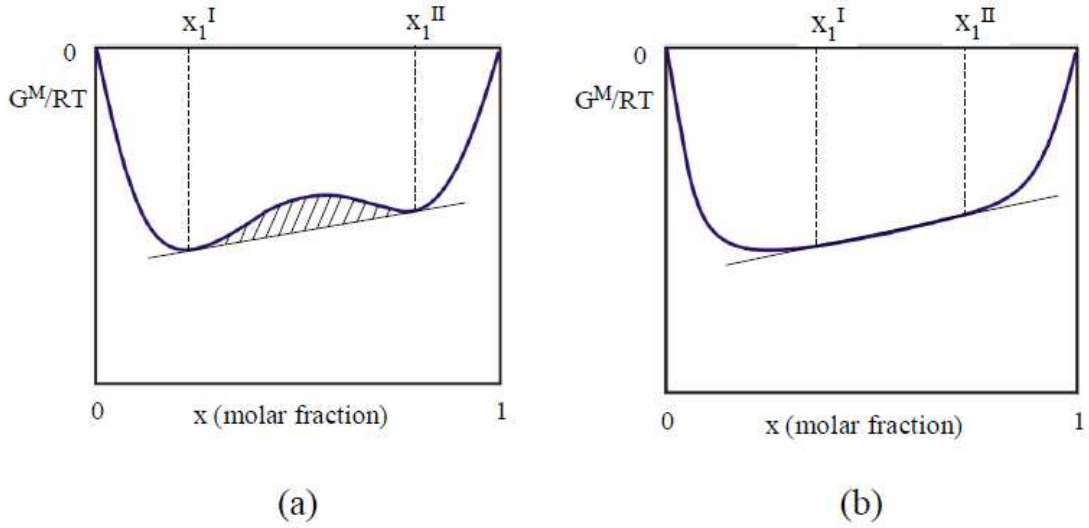


Figure 1. Different possibilities for the dimensionless Gibbs energy of mixing (G^M/RT) for a binary system: a) good definition, and b) poor definition of the LL equilibrium points.

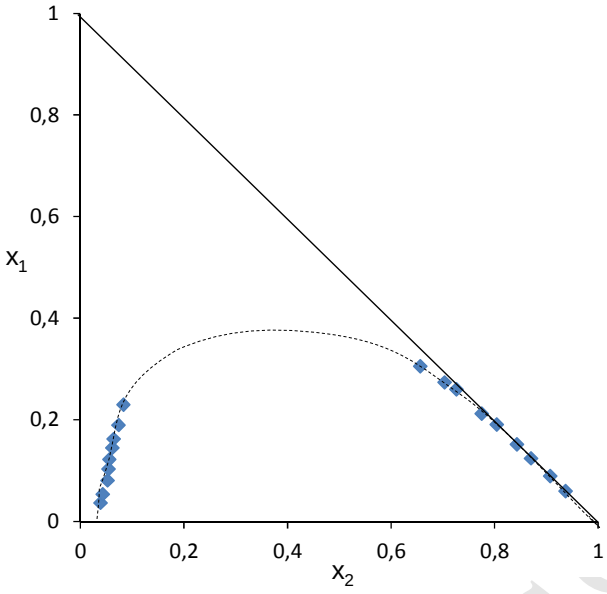
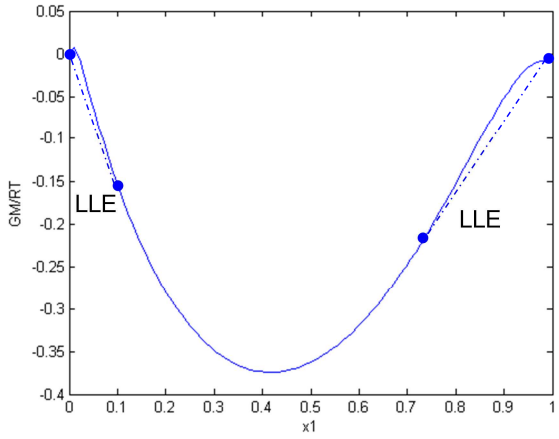
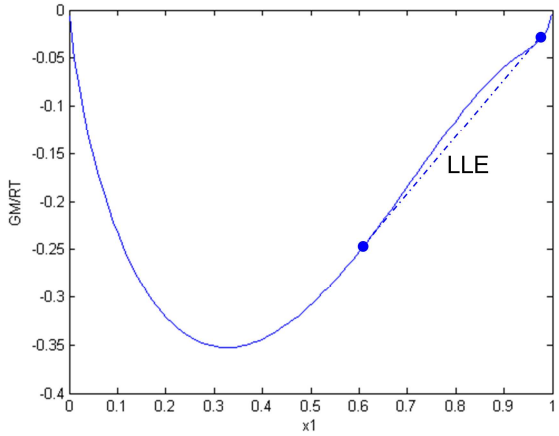


Figure 2. Tie-line data for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) type I ternary system at T=298.15 K (case 1): ◆, experimental value; ---, approximate binodal curve.

a)



b)



c)

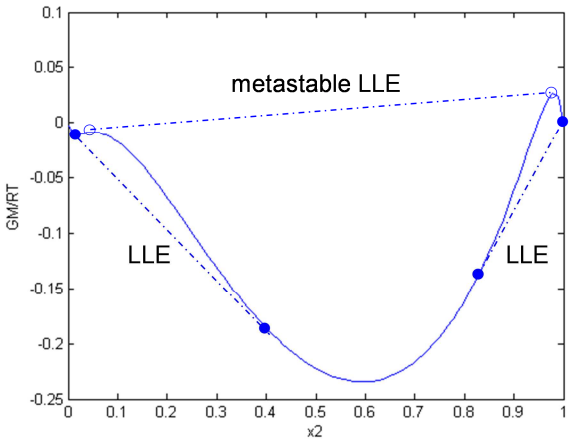
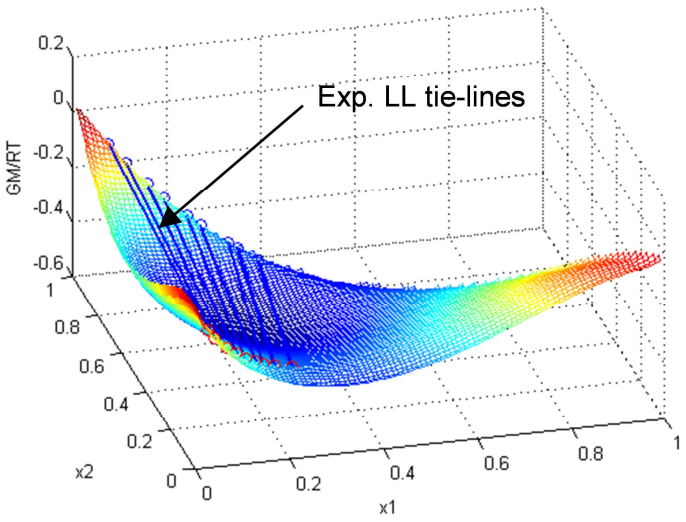


Figure 3. Representation of the G^M/RT function for each one of the three binary subsystems for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) ternary system at T=298.15 K (case 1), using the NRTL model with the parameter values shown in Table 2a: a) binary (1)-(2); b) binary (1)-(3), and c) binary (2)-(3).

a)



b)

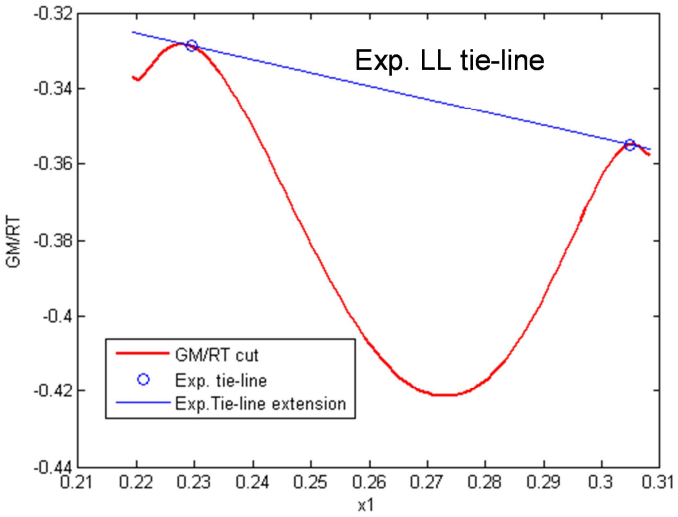
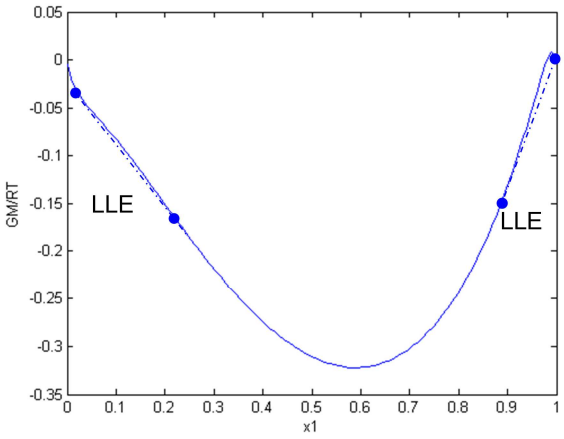
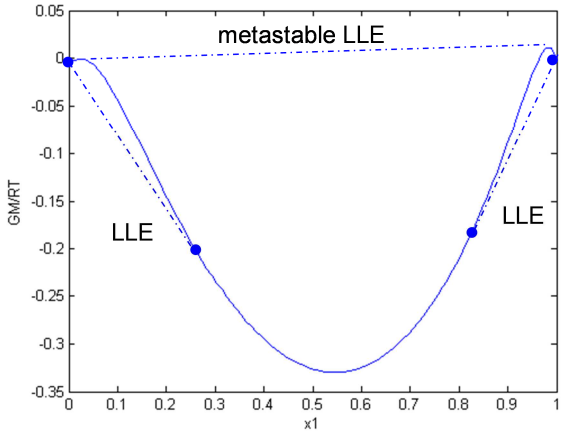


Figure 4. Calculated G^M/RT surface (NRTL model with the parameter values in Table 1a) and experimental LLE tie-lines for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) ternary system at T=298.15 K (case 1): a) 3D representation, and b) sectional plane in the direction defined by the ternary tie-line #9.

a)



b)



c)

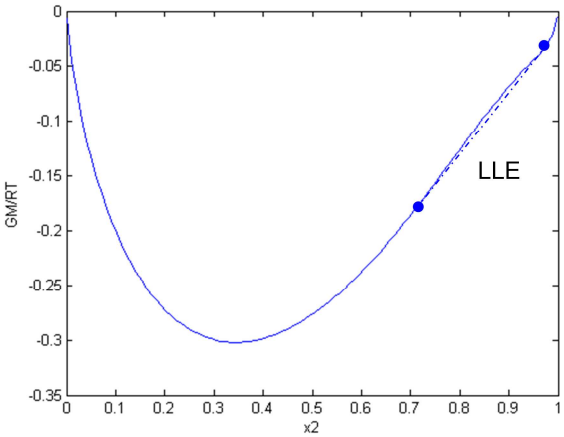


Figure 5. Representation of the G^M/RT function for each one of the three binary subsystems for the n-hexane (1) + benzene (2) + sulfolane (3) ternary system at 298.15K (case 2), using the NRTL model with the parameter values shown in Table 3a: a) binary (1)-(2); b) binary (1)-(3), and c) binary (2)-(3).

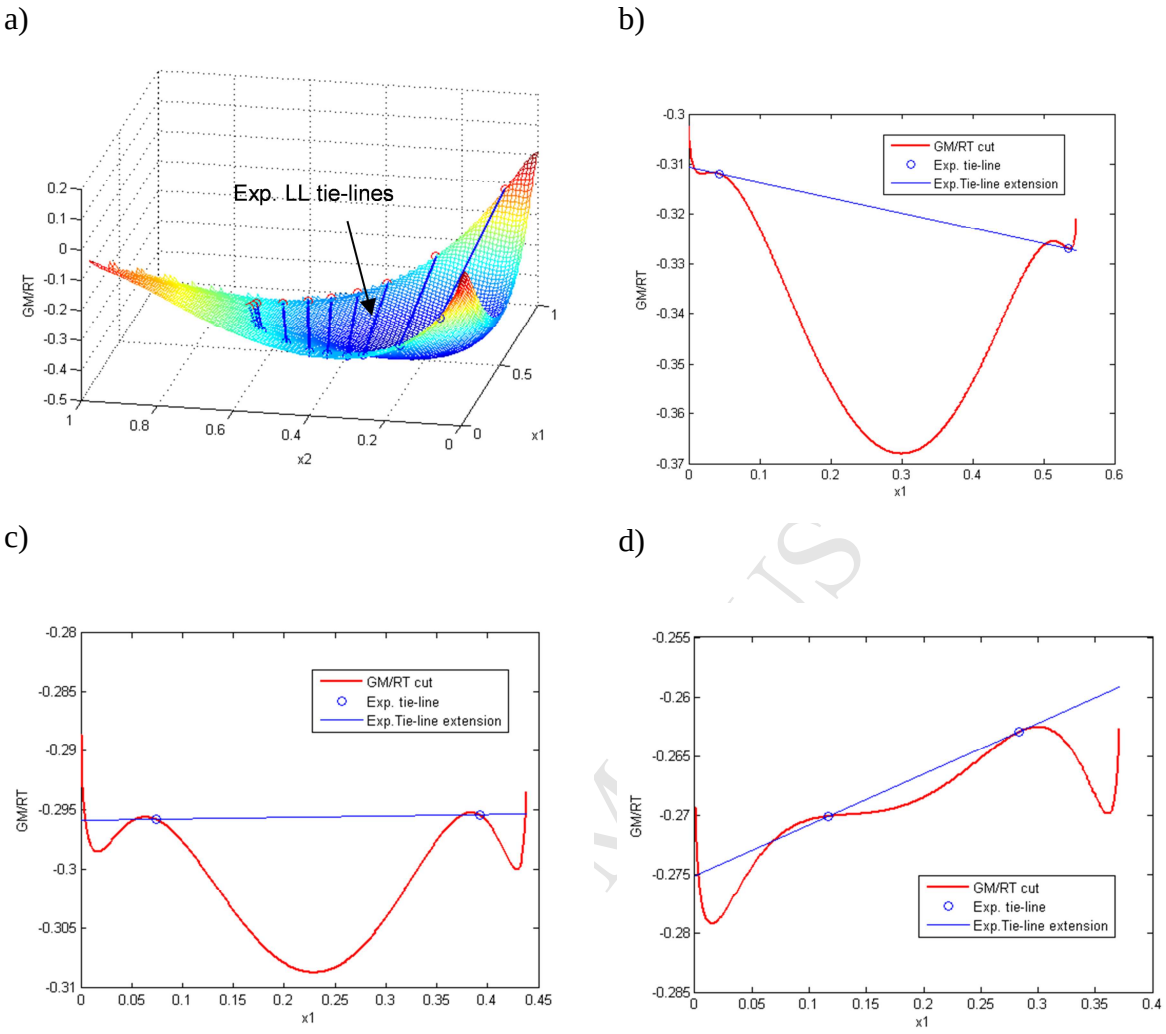
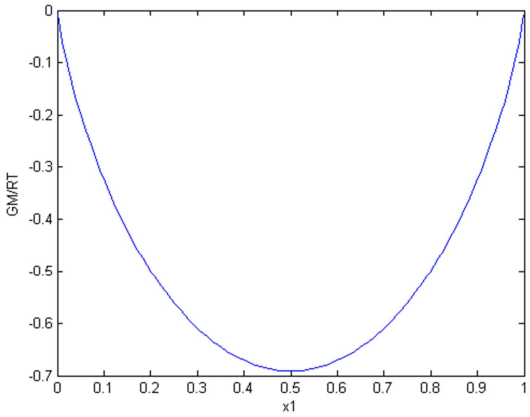
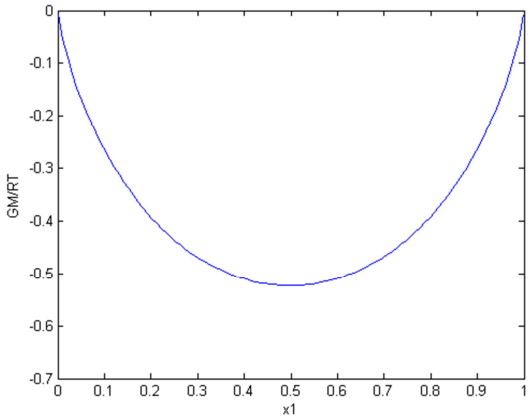


Figure 6. Calculated G^M/RT surface (NRTL model with the parameter values in Table 2a) and experimental LLE tie-lines for the n-hexane (1) + benzene (2) + sulfolane (3) ternary system at 298.15K (case 2): a) 3D representation, and b-d) sectional planes in the directions defined by the ternary tie-lines #5, #7 and #9, respectively.

a)



b)



c)

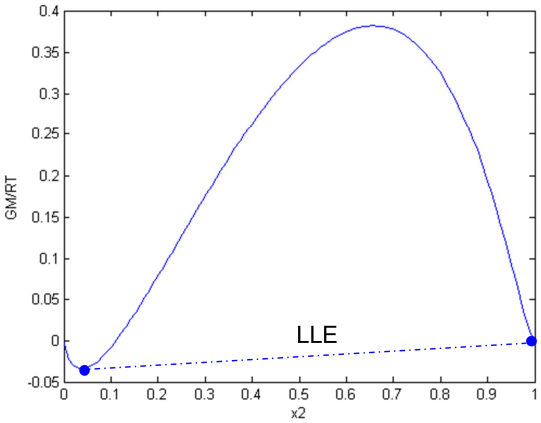
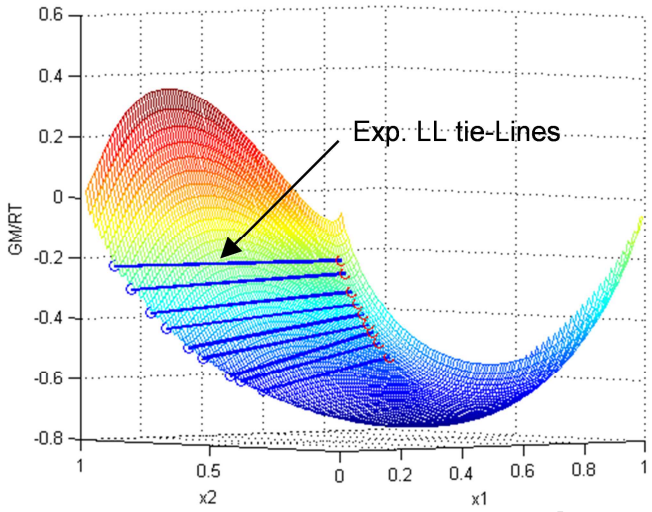


Figure 7. Representation of the G^M/RT function for each one of the three binary subsystems for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) ternary system at T=298.15 K (case 1), obtained in the present paper by LLE correlation using the NRTL model with the parameter values shown in Table 2b: a) binary (1)-(2); b) binary (1)-(3), and c) binary (2)-(3).

a)



b)

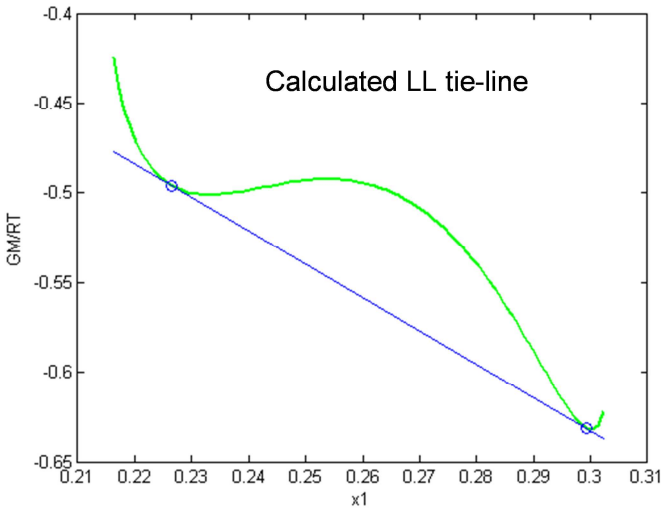


Figure 8. Calculated G^M/RT surface (NRTL model with the parameter values in Table 1b) and experimental LLE tie-lines for the benzene (1) + cyclohexane (2) + dimethyl sulfoxide (DMSO) (3) ternary system at T=298.15 K (case 1): a) 3D representation, and b) sectional plane in the direction defined by the ternary tie-line #9.